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## MÖSSBAUER STUDIES OF ICELANDIC LAVAS

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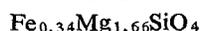
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**Résumé.** — Deux échantillons de lave d'Islande ont été étudiés par la spectroscopie Mössbauer. On a trouvé qu'une haute vitesse de solidification cause un plus petit éclatement quadripolaire des ions  $\text{Fe}^{2+}$ . Un des échantillons contient des particules superparamagnétiques. Une température de transition magnétique de l'olivine  $\text{Fe}_{0,34}\text{Mg}_{1,66}\text{SiO}_4$  est observée entre 5 K et 11 K.

**Abstract.** — Two samples of lava from Iceland have been studied by use of Mössbauer spectroscopy. It is found that a high rate of solidification leads to smaller quadrupole splittings of the ferrous doublets. One of the samples contains superparamagnetic particles. The olivine



becomes magnetically ordered between 5 K and 11 K.

**1. Introduction.** — The iron content of many minerals makes Mössbauer spectroscopy a valuable tool for the study of geological samples. In a number of Mössbauer studies [1-5] the site populations of  $\text{Fe}^{2+}$  ions in the M1 and M2 sites of olivine,  $(\text{Fe}_x\text{Mg}_{1-x})_2\text{SiO}_4$ , and pyroxene,  $\text{Fe}_x\text{Mg}_{1-x}\text{SiO}_3$ , have been investigated.

Mössbauer spectroscopy is particularly valuable in the study of amorphous and microcrystalline samples which are not easily studied by use of other methods. In the present study we have examined two samples of Icelandic lava with special reference to the investigation of microcrystalline and amorphous fractions. One of them, Sample 1, is from the lavafield Budarhraun in western Iceland. It contains crystals of olivine and pyroxene, and a large amount of microcrystalline material. The second sample, Sample 2, is a volcanic bomb, i. e. a lump of lava (approx. 25 cm in diameter with a central cavity of about 5 cm in diameter) which was thrown out of the volcano Hekla at an early stage of its eruption in 1947. The bomb, which is described elsewhere [6] shows clear evidence of fast cooling on the surface and slower solidification of the interior.

**2. Experimental.** — By magnetic separation in a Franz isodynamic separator combined with gravi-

metric separation in heavy liquids. Sample 1 was separated into three fractions: the olivine crystals, the pyroxene crystals, and the remaining microcrystalline fraction. The chemical composition was determined by electron microprobe. Six absorbers were prepared of Sample 2, taken at uniform intervals from the surface of the bomb to its centre. The Mössbauer spectra were obtained by using conventional constant acceleration spectrometers with sources of  $^{57}\text{Co}$  in Pd and Rh.

**3. Results.** — 3.1. SAMPLE 1 (Lava from Budarhraun). — Figures 1, 2, and 3 show some spectra of the separated fractions of Sample 1. The spectra shown in figures 1 and 2 were obtained at 368 K and 80 K, respectively. The spectra of pyroxene (1*b* and 2*b*) and olivine (1*c* and 2*c*) show that the M1 and M2 quadrupole doublets of olivine are only resolved above 300 K, whereas the M1 and M2 doublets of pyroxene are better resolved at low temperatures. The room temperature Mössbauer parameters of the olivine and the pyroxene are given in Table 1.

The spectra of the microcrystalline fraction (1*a* and 2*a*) show distinct lines corresponding to those of the separated olivine and pyroxene. Moreover, these spectra contain absorption lines characteristic of ilmenite ( $\text{FeTiO}_3$ ) (e. g. the line at 1.3 mm/s in the 368 K spectrum). The large number of partly overlapping lines prevents an unambiguous determination of the line positions and areas. However, it is note-

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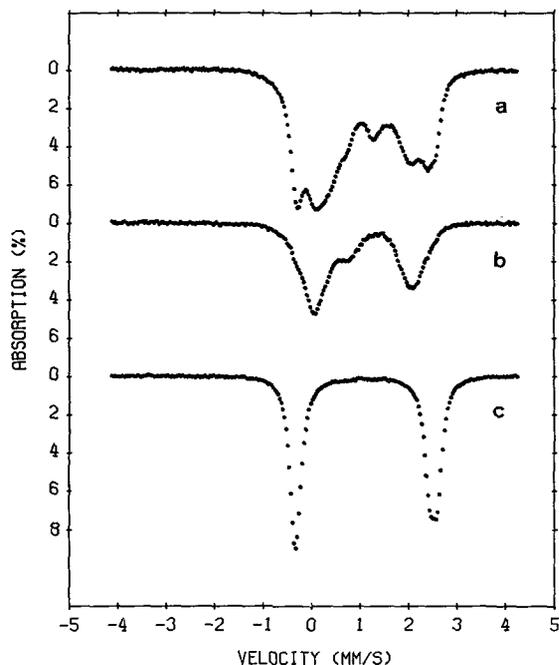


FIG. 1. — Mössbauer spectra of the separated fractions of Sample 1 at 368 K. *a*: Microcrystalline fraction. *b*: Pyroxene. *c*: Olivine.

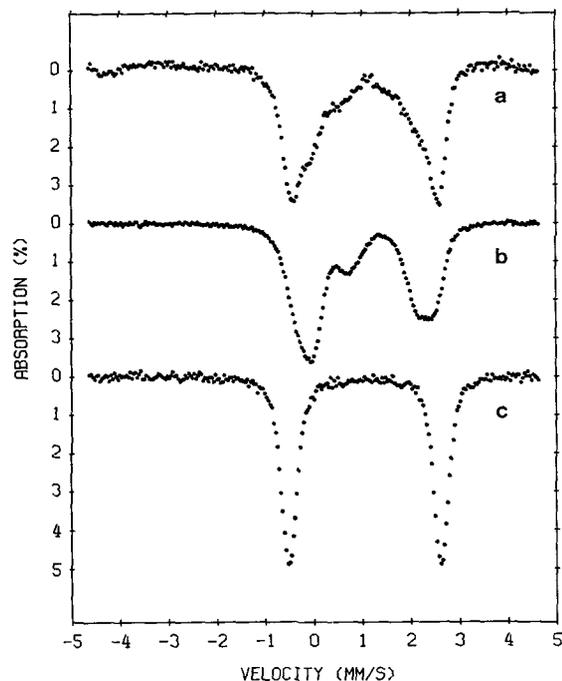


FIG. 2. — Mössbauer spectra of the separated fractions of Sample 1 at 80 K. *a*: Microcrystalline. *b*: Pyroxene. *c*: Olivine.

worthy that the resolution improves with increasing temperatures. It was found that at all temperatures the olivine spectrum of the microcrystalline sample showed a quadrupole splitting which is about 0.15 mm/s smaller than that of separated olivine crystals.

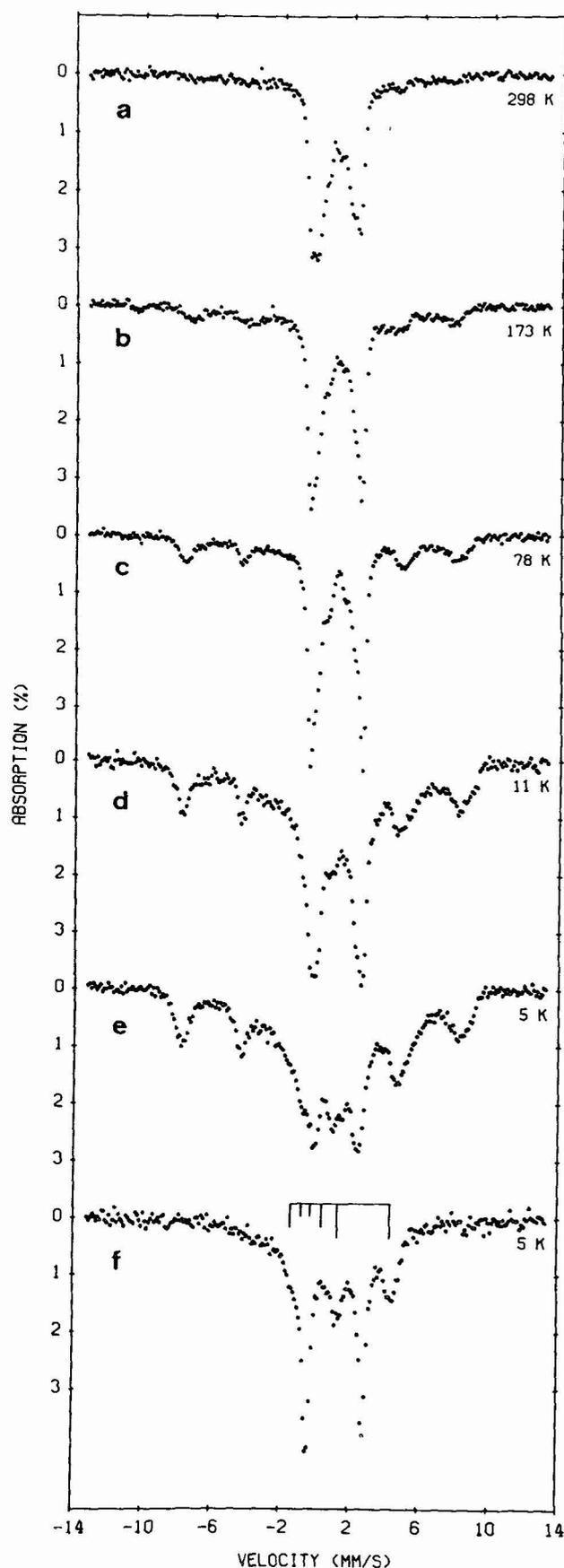
Figure 3*a-e* shows spectra of the microcrystalline fraction in a large velocity range. It is noticeable that the area of the magnetically split component increases with decreasing temperatures. This indicates the presence of superparamagnetic particles. The hyperfine field of this component is about 500 kOe at 11 K. The relative intensities of the lines did not change significantly when a magnetic field of 12 kOe was applied perpendicular to the gamma ray direction at 78 K. Therefore, the particles are probably antiferromagnetic. The value of the hyperfine field is slightly smaller than that of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. Moreover, some of the lines are quite broad, even at 11 K. This suggests that the particles consist of a mixed oxide. Between 11 K and 5 K the spectrum changes considerably. The changes can be interpreted by a magnetic ordering in microcrystals of

olivine in the absorber. This is confirmed by the spectrum of the separated olivine at 5 K (spectrum 3f) which shows absorption lines similar to the new lines which develop in the spectra of the microcrystalline fraction between 11 K and 5 K. The spectrum 3f can be interpreted in terms of a hyperfine field of about 100 kOe at one of the two iron positions and a much smaller hyperfine field at the other one. In pure fayalite, Fe<sub>2</sub>SiO<sub>4</sub>, the two Fe<sup>2+</sup> positions show hyperfine fields of 323 kOe and 120 kOe, respectively, at 9 K [7]. Fayalite has a magnetic transition temperature of 66 K [7]. An analysis of the present olivine with electron microprobe showed the composition Fe<sub>0.34</sub>Mg<sub>1.66</sub>SiO<sub>4</sub>. The transition temperature between 11 K and 5 K can therefore be explained by the presence of diamagnetic ions, Mg<sup>2+</sup>, substituting Fe<sup>2+</sup> in Fe<sub>2</sub>SiO<sub>4</sub>. There is no indication of magnetic ordering in the pyroxene, which was found to have the composition Mg<sub>0.45</sub>Fe<sub>0.10</sub>Ca<sub>0.45</sub>SiO<sub>3</sub>, clinopyroxene. This is consistent with an earlier study [8] which showed that in (Fe<sub>x</sub>Mg<sub>1-x</sub>)SiO<sub>3</sub> the magnetic transition temperature is lower than 1.7 K for  $x < 0.39$ .

TABLE I

Mössbauer parameters of separated minerals of Sample 1 at 298 K

	$\delta_{\text{Fe}}$ (mm/s)	$\Delta$ (mm/s)	$\Gamma$ (mm/s)	Fractional area (%)
Olivine (M1 + M2)	1.13	2.94	0.34	100
Pyroxene (Fe <sup>3+</sup> )	0.46	0.71	0.50	25 ± 3
Pyroxene (Fe <sup>2+</sup> ) (M1)	1.10	2.37	0.54	43 ± 3
Pyroxene (Fe <sup>2+</sup> ) (M2)	1.12	1.86	0.44	32 ± 3



3.2 SAMPLE 2 (The volcanic bomb). — The structure of the bomb was investigated with x-ray diffraction. The measurements showed evidence of a few well-developed crystals in the surface as well as in the central part. Besides, both fractions showed the presence of large amounts of amorphous material. The central part of the bomb was found also to contain microcrystalline material.

Scanning electron micrographs of a sample from the central part did not show any indication of crystalline material, even at 30 000 times magnification. The micrograph, figure 4, shows that the needle-shaped

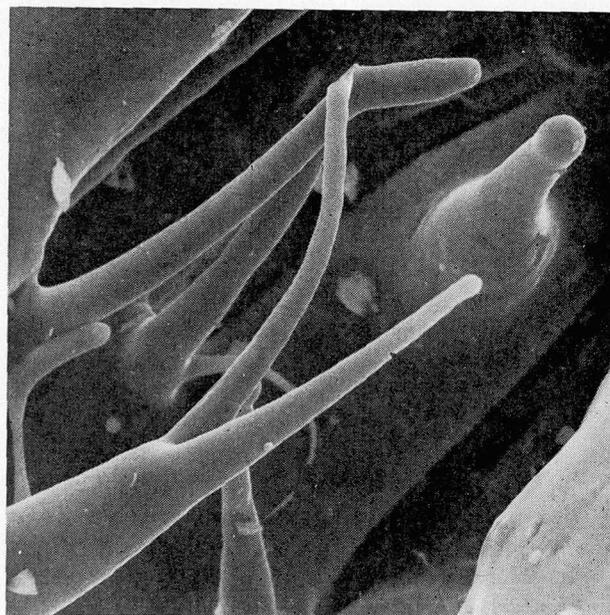


FIG. 4. — Scanning electron micrograph of structures from the centre of the volcanic bomb (900 × magnification).

structures which are present in the interior of the bomb are not single crystals as might be expected.

Figure 5 shows Mössbauer spectra of fractions from the central part and the surface at 80 K. Only small differences between the spectra can be seen. By use of the stripping technique [9], the surface spectrum being subtracted from the others, it was found that the spectra of the samples from below the surface were identical. However, the surface spectrum shows slightly smaller quadrupole splittings ( $\sim 0.1$  mm/s) of the  $\text{Fe}^{2+}$  doublets. This difference was also found by a conventional computer fitting procedure, although the splittings showed a small dependence on the constraints used. It was found that the surface contains a slightly larger amount of  $\text{Fe}^{3+}$  than the interior (approx. 12 % and

FIG. 3. — *a-e*: Mössbauer spectra of the microcrystalline fraction of Sample 1 at various temperatures. *f*: spectrum of the separated olivine at 5 K. The bar diagram indicates an interpretation of the positions of the weak lines in terms of a hyperfine field of 100 kOe at one of the two  $\text{Fe}^{2+}$  sites.

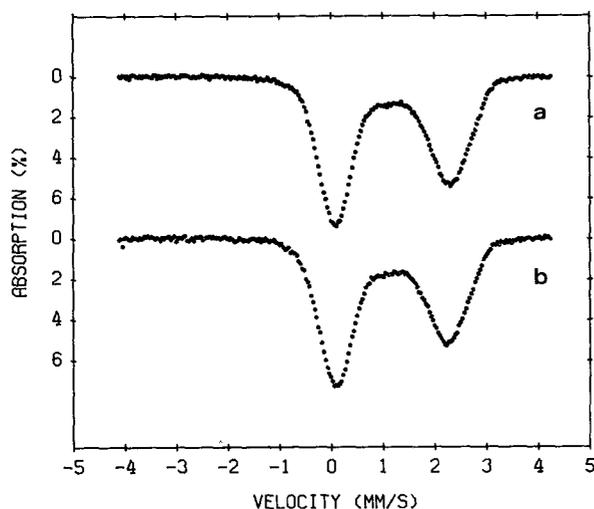


FIG. 5. — Mössbauer spectra of the volcanic bomb at 80 K. *a*: Central fraction. *b*: Surface fraction.

10 %, respectively). A conventional chemical analysis showed the same tendency with somewhat higher amounts of  $\text{Fe}^{3+}$  (approx. 20 % and 18 %, respectively).

**4. Discussion.** — The surface layer of Sample 2 and the microcrystalline fraction of Sample 1 both show a tendency towards a smaller quadrupole splitting of the  $\text{Fe}^{2+}$  doublets. Both these fractions have probably solidified faster than the remaining fractions of the samples. Generally, the quadrupole splitting of ferrous ions decreases with increasing distortion of the surroundings [10]. The fast solidified fractions of the samples therefore seem to have a more distorted structure than the remaining parts of the samples. In crystalline samples such distortions may be induced by lattice defects, by disordering of the cations or by the presence of different cations, substituting for instance  $\text{Fe}^{2+}$  or  $\text{Mg}^{2+}$  in olivine.

The higher amount of  $\text{Fe}^{3+}$  at the surface of the bomb is presumably due to the oxidation of the surface during the passage of the glowing lava through

the atmosphere. The magnetic phase transition between 5 K and 11 K of the present olivine, which is near the forsterite ( $\text{Mg}_2\text{SiO}_4$ ) in the fayalite-forsterite series, shows that olivines containing a considerable amount of diamagnetic ions also become magnetically ordered above helium temperature. The similarity of the magnetically split lines of the separated olivine and the olivine in the microcrystalline fraction (Fig. 3e and 3f) shows that these olivine crystals have similar magnetizations at 5 K. This indicates that the microcrystalline olivine has a composition similar to that of the separated olivine.

The superparamagnetic behaviour of the oxide in Sample 1 may give some information on the particle size of the oxides. By comparison with Mössbauer spectra of  $\alpha\text{-Fe}_2\text{O}_3$  particles [11] and assuming a similar anisotropy constant we find a particle size of about 60 Å.

**5. Conclusion.** — The present study demonstrates that Mössbauer spectroscopy gives a considerable amount of information on geological samples which are not easily studied by other methods. Although the large number of overlapping lines may prevent an unambiguous computer analysis several features of microcrystalline and amorphous samples can be studied, especially when spectra are obtained at various temperatures.

The application of the conventional stripping technique (subtraction of known spectra of minerals from the experimental spectra) seems to be of limited value here, as the minerals from various fractions of the samples have different Mössbauer parameters. In particular the quadrupole interaction has been shown to differ for different fractions of the sample, probably due to distortions in the fast solidified fractions. However, in some cases, e. g. when comparing similar spectra, the stripping technique can conveniently be used for tracing small differences.

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